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(71)Applicant : MITSUBISHI MATERIALS CORP

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(72)Inventor : MORI AKIRA  
SOYAMA NOBUYUKI  
KAGEYAMA KENSUKE

## (54) SOLUTION FOR FORMING THIN OXIDE FILM

### (57)Abstract

**PROBLEM TO BE SOLVED:** To improve the preservation stability and to prevent the formation of a precipitate even when a soln. is preserved for a long period by incorporating the respective carboxylates of La, Sr and Co into an org. solvent in a specified molar ratio and further specifying the concns. of the respective metals and the water content of the soln.

**SOLUTION:** Respective carboxylates of La, Sr and Co are incorporated into an org. solvent in a molar ratio corresponding to  $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$  (where  $0.1 \leq x \leq 0.6$ ). The content of La is controlled to  $\leq 8$  wt.%, that of Sr to  $\leq 10$  wt.% and that of Co to  $\leq 10$  wt.%, and the water content is controlled to  $\leq 1$  wt.% to prepare a soln. for forming the thin film of an LaSrCo multiple oxide. The soln. is applied on a substrate and heated to form a thin oxide film. The thin oxide film is heat-treated and crystallized to form the thin film of the LaSrCo multiple oxide having a perovskite structure. A hydrocarbonic solvent immiscible with water is preferably used as the org. solvent.

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CLAIMS	DETAILED DESCRIPTION	TECHNICAL FIELD	PRIOR ART	EFFECT OF THE INVENTION	TECHNICAL PROBLEM	MEANS
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XAMPLE

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Claim(s)]

Claim 1] the inside of an organic solvent — each of a lanthanum, strontium, and cobalt — the solution for LaSrCo multiple oxide thin film formation which consists of a solution which contains carboxylate by the mole fraction corresponding to formula:  $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$  ( $0.1 \leq x \leq 0.6$ ), and is characterized by for the concentration of each metal in a solution being less than [ La:8 % of the weight ], less than [ Sr:10 % of the weight ], and less than [ Co:10 % of the weight ], and the moisture concentration of a solution being 1 or less % of the weight.

Claim 2] The membrane formation approach of a LaSrCo multiple oxide thin film including the process which applies the solution for thin film formation of claim 1 to a base, the process which heats a paint film and forms an oxide thin film, and the process which heats the obtained oxide thin film and is crystallized.

Claim 3] The LaSrCo multiple oxide thin film with the perovskite crystal structure formed from the solution for oxide thin film formation according to claim 1.

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## ETAILED DESCRIPTION

### Detailed Description of the Invention]

001]

Field of the Invention] This invention is the multiple oxide of the perovskite crystal structure containing a lanthanum, strontium, and cobalt (a LaSrCo multiple oxide or LSCO, and brief sketch) It is related with the membrane formation approach of an oxide thin film and the obtained oxide thin film using the solution for oxide thin film formation for forming a thin film with a wet method, i.e., a sol-gel method, and this solution. The formed oxide thin film is useful although the thin film for electrodes of semiconductor memory, such as ferroelectric nonvolatile memory, is formed.

002]

Description of the Prior Art] DRAM currently used for the current Lord as rewritable memory is volatile memory, it is necessary to pass a current periodically because of storage maintenance, and it has been a problem from the environmental side that power consumption is large. Then, it is nonvolatile, since storage can be held for a long period of time, there is little power consumption, and the ferroelectric random-access memory which is compatible with DRAM attracts attention. Ferroelectric random-access memory replaces the capacitor part of DRAM with a ferroelectric thin film, and gives a memory storage function to this thin film using the hysteresis phenomenon of the spontaneous polarization of a ferroelectric. PZT ( $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ,  $0 < x < 1$ ) with large spontaneous polarization as a ferroelectric thin film material of this ferroelectric random-access memory etc. — the perovskite mold oxide ingredient and the stratified superlattice mold oxide ingredient are suitable.

003] In order to form the thin film of these oxide ingredients, heat treatment in an oxidizing atmosphere is needed for crystallization. In that case, a front face oxidizes that a lower electrode is the usual metal, and a device property deteriorates remarkably. Therefore, noble platinum is conventionally used as an electrode material chemically.

004] since [ however, ] platinum has the trouble that the adhesion with  $\text{SiO}_2$  which is not good is bad — ruthenium oxide ( $\text{RuO}_2$ ) etc. — the oxide electrode which consists of a noble-metals oxide has come to be tried as an electrode of nonvolatile memory. It is said that an oxide electrode can improve the fatigue resistance of this thin film remarkably when the oxygen deficiency of the ferroelectric thin film which is the memory ingredient of a ferroelectric can be prevented.

005] as the ingredient of such an oxide electrode — Jpn.J.Appl.Phys.Vol. — 37 (1998) and pp.L936-38 \*\*\*\* —  $\text{MgO}$  Forming the ZT ferroelectric capacitor thin film which used upwards the electrode which consists of a LaSrCo multiple oxide with a sol-gel method is reported. The solution of commercial 0.25 M concentration is used for membrane formation of a LaSrCo multiple oxide.

006] Unlike the gaseous-phase forming-membranes methods, such as the sputtering method, the laser ablation method, and reactant vacuum deposition, in addition to the advantage that it is easy and suitable for mass production, presentation control of the film is easy for the wet forming-membranes methods, such as a sol-gel method, and they have the features that membrane formation thickness is comparatively uniform.

007]

Problem(s) to be Solved by the Invention] However, the sol-Ringer's injection for LaSrCo multiple oxide membrane formation by which current marketing is carried out has low preservation stability, and precipitate is produced in about one month. If the solution which produced precipitate even when it was very small is used, the electrical property of the obtained film becomes heterogeneous, and since the dependability of a product is spoiled greatly, it cannot but discard. Therefore, there was much futility and an improvement of the preservation stability of a solution was desired. This invention makes it a technical problem to offer the solution for oxide thin film formation for LaSrCo multiple oxide membrane formation which does not produce precipitate even if preservation stability improves remarkably from elegance conventionally, for example, it carries out a mothball.

008]

Means for Solving the Problem] As a result of repeating examination that the above-mentioned technical problem should be solved, this invention persons used carboxylate as a source of supply of each metal, are restricting the atomic ratio of La and Sr, and the concentration and moisture concentration of each metal carboxylate in a solution, knew that the above-mentioned technical problem could be solvable, and completed this invention.

009] A lanthanum, strontium, and cobalt this invention each in an organic solvent here carboxylate Formula : It consists of a solution obtained by the mole fraction corresponding to  $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$  ( $0.1 \leq x \leq 0.6$ ). It is the solution for LaSrCo multiple oxide thin film formation characterized by for the concentration of each metal in a solution being less than [ La:8 % of the weight ], less than [ Sr:10 % of the weight ], and less than [ Co:10 % of the weight ], and the moisture concentration of a solution being 1 or less % of the weight.

010] According to this invention, the membrane formation approach of the oxide thin film which includes the process which applies the above-mentioned solution for oxide thin film formation to a base, the process which heats a paint film and forms an oxide thin film, and the process which heat-treats the obtained oxide thin film and is crystallized again is offered. Moreover, the thin film of a LaSrCo multiple oxide with the perovskite crystal structure formed from the above-mentioned solution for oxide thin film formation is also offered by this invention.

011]

[Embodiment of the Invention] The thin film formed with the solution for oxide thin film formation of this invention is a multiple oxide containing La, and Sr and Co. (namely, a LaSrCo multiple oxide or LSCO) It is a thin film. This multiple oxide may be contained if other metallic elements are little in addition to La, Sr, and Co. Ce, Pr, Nb, Rh, and Ir are mentioned as an example of other metallic elements which are made to contain and it deals.

012] Since a LaSrCo multiple oxide is generally the conductive ingredient of low resistance, the thin film of this multiple oxide may function as an oxide electrode. However, especially the application of a thin film is not restricted in this invention. It can also be used for other applications [ say / the barrier layer made to intervene between an electrode and a ferroelectric capacitor in addition to an electrode ].

013] As for a desirable multiple oxide, a metallic element serves as La only from Sr and Co. such a multiple oxide — general —  $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$  ( $0 < x < 1$ ) — although it can express with a formula — this invention —  $x$  values — 0.1–0.6 It considers as the range.  $x$  values are 0.1. The following or 0.6 super-\*\*\*\*\*, and the storage stability of liquid fall, and it becomes easy to generate precipitate during storage. In addition,  $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$  Generally in the film, the surface electrical resistance of a thin film is changed by fluctuation of  $x$  values within the limits of  $10^{-4}$  –  $10^{-1}$  ohm-cm base.

014] The solution for oxide thin film formation of this invention contains each metal which constitutes the multiple oxide which should form membranes, i.e., the oxide precursor of La, Sr, and Co\*\*. An oxide precursor is a compound which changes with heating to an oxide. As this common kind of an oxide precursor, although a metal alkoxide, a metal acetylacetonato complex, metal carboxylate, etc. are often used, by this invention, carboxylate is used about both La, and Sr and Co. If an alkoxide and an acetylacetonato complex are used, it will become easy to generate precipitation during liquid storage.

015] Although especially the carboxylate used as an oxide precursor of each metal is not restricted, the salt of the carboxylic acid of carbon numbers 1–10, for example, acetate, propionate, butyrate, a hexane salt, 2-ethyl hexane salt, an octanoic-acid salt, a decanoic-acid salt, etc. are desirable. It is 2-ethyl hexanoic-acid salt which pyrolyzes especially desirable carboxylate at low temperature comparatively about every metal of La, Sr, and Co.

016] The oxide precursor of each metal of a raw material, i.e., each carboxylate of La, and Sr and Co, (the oxide precursor of other metals can also be used by the case) Predetermined metal atomic ratio (namely, shown by  $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$   $x$  within the limits of 0.1–0.6) If it is made to dissolve in a suitable organic solvent by the mole ratio to produce, the solution for oxide thin film formation will be obtained.

017] Although the solvent of water miscibilities, such as alcohol and a ketone, can also be used as an organic solvent, an organic solvent of water immiscibility like a hydrocarbon system solvent is desirable. As an example of a desirable organic solvent, aliphatic series or alicyclic hydrocarbon, such as aromatic hydrocarbon, such as benzene, toluene, and a xylene, a hexane, an octane, and a cyclohexane, etc. are mentioned.

018] Only by dissolving the metal carboxylate of a raw material in an organic solvent by the predetermined ratio, the obtained solution is lacking in stability, and precipitate generates it within a short period of time, and it becomes impossible however, to use it for membrane formation. Therefore, in this invention, the concentration and moisture concentration of each metallic compounds in a solution are restricted. That is, as a content of metal conversion, La in a solution and concentration of each carboxylate of Sr and Co are made into less than [ La:8 % of the weight ], less than [ Sr:10 % of the weight ], and less than [ Co:10 % of the weight ], and the moisture concentration of a solution carries out them to 1 or less % of the weight. This metal concentration is less than [ La:2 % of the weight ], less than [ Sr:3 % of the weight ], and less than [ Co:3 % of the weight ] preferably. The moisture concentration in a solution is 0.5 preferably. It carries out to below weight %. If either of each metal concentration or moisture concentration in a solution exceeds the above-mentioned upper limit, the stability of a solution will fall and a mothball will become difficult.

019] The concentration of each metal carboxylate is the amount of the organic solvent used. (namely, dilution by the organic solvent) can adjust easily. About moisture, since the metal carboxylate of a raw material generally has water of crystallization, the solution which dissolved this contains the moisture originating in the water of crystallization of carboxylate. Furthermore, when an organic solvent is a solvent with a high water miscibility like alcohol or a ketone, if it is left, the moisture in air will be absorbed and the moisture concentration of a solution will increase. Therefore, the moisture mixed into a solution by such cause will be removed.

020] What is necessary is to heat under reduced pressure preferably and for evaporation or distillation just to remove water, after dissolving the metal carboxylate of a raw material in an organic solvent, in order to remove the moisture introduced by the water of crystallization etc. into a solution from the metal carboxylate of a raw material and to dehydrate a solution. In this case, as an organic solvent, it is more desirable than water that the boiling point uses a high thing. the case where an organic solvent is water immiscibility although it may be performed making this heating condense without flowing back — reflux heating (that is, the organic solvent which remains after separating water from a distillate is flowed back — making) It can also carry out. Heating time is set up so that moisture may be removed nearly completely.

021] Thus, the solution of the dehydrated metal carboxylate is diluted with an organic solvent if needed, and concentration is adjusted. The organic solvent used for the dissolution and dilution of a raw material of metal carboxylate has the desirable thing of water immiscibility, as mentioned above. It is because the organic solvent of the water miscibility represented with alcohol tends to absorb moisture during preservation and use and a solution tends to become unstable.

022] The solution for oxide thin film formation concerning this invention can be saved at stability, without producing precipitate substantially over the long period of time beyond several months thru/or one year, or it, if sealed and saved. Therefore, according to a sol-gel method, the thin film of a LaSrCo multiple oxide can be easily formed using this solution.

023] Membrane formation actuation is the same as that of the conventional sol-gel method, and is good. First, the above-mentioned solution is applied on a base. Although spreading is usually performed with a spin coat method, other applying methods, such as roll coating, spraying, immersion, and a doctor blade, are applicable. A paint film is dried after spreading if needed, and a solvent is removed. Although this drying temperature changes also with classes of solvent — usually — 80 – 200 °C extent — it is — for example, — It is good in the range of 100 – 180 °C. However, since a solvent is removed in the temperature up in the case of heating for making it

convert into the following metallic oxide, the desiccation process of a paint film is necessarily unnecessary.

0024] Then, heat the applied base, the metallic compounds of a precursor are made to convert into a metallic oxide, and the film which consists of a metallic oxide is formed. Although especially a heating ambient atmosphere is not restricted, it is usually air. Generally it is heating temperature. It is the range of 300 - 400 \*\*, and heating time is a 1 - 15-minute about room.

0025] When not becoming thickness required of one spreading, it is the above-mentioned spreading. (desiccation) Heating is repeated and the film of the metallic oxide of desired thickness is obtained. In this way, since the obtained film is amorphous, or its crystallinity is inadequate and its conductivity is inadequate, it is not suitable for using it as an electrode.

0026] Therefore, finally, it heat-treats at the temperature beyond the crystallization temperature of the metallic oxide, and considers the metallic-oxide thin film of a crystalline substance with the crystal structure of a perovskite mold. In addition, although heat treatment for crystallization finally may not be performed by once but you may carry out after the above-mentioned heating for every each applied paint film, it is economically more advantageous to carry out by collecting at the end, since it is necessary to repeat heat treatment in an elevated temperature repeatedly.

0027] The heat treatment temperature for this crystallization is usual. It is the range of 650 - 800 \*\*. The heat treatment time amount for crystallization is usually 1 minute - about 1 hour, and although especially a heat treatment ambient atmosphere is not restricted, it is usually air.

0028] Thus, although the thin film of the formed LaSrCo multiple oxide is useful as the oxide electrode and barrier layer of a ferroelectric RAM as mentioned above for example, since it is excellent in conductivity, an application is not restricted to this.

0029] Example] 2-ethyl hexanoic-acid lanthanum and 2-ethyl hexanoic-acid strontium which have water of crystallization, respectively, and 2-ethyl hexanoic-acid cobalt were dissolved in the xylene at a rate which produces a predetermined metal atomic ratio, and the solution of 10 % of the weight of solid content was prepared. It is under reduced pressure of 100 Torr, stirring this solution by the stirrer in an eggplant flask. It heated and condensed by 110 - 120 \*\*, and moisture was removed. Heating time was changed and the solution with which moisture concentration differs was obtained. After cooling the obtained concentration liquid radiationally to a room temperature, it diluted with the xylene to predetermined concentration, and the solution for LaSrCo multiple oxide film formation was obtained. The moisture concentration of the obtained solution was measured by Karl Fischer titration.

0030] Each solution was sealed in the glass bottle, and was kept for three months at the room temperature, and the existence of precipitate generating after storage was observed visually. About a result, they are La in a solution, Sr, and cobalt group conversion concentration. (it analyzes by the ICP method) And with moisture concentration, it is shown in Table 1. In Table 1, the underline section is the value of this invention out of range.

0031] Each solution before storage was used and the oxide thin film shown by formula:La0.5Sr0.5CoO3 of perovskite type structure on silicon substrate with an oxide film was formed. Membrane formation is in the air after applying a solution with a spin coat method. Desiccation for [ 300 degree-Cx ] 3 minutes It is in air to a crystallization sake in the last after forming an oxide thin film with heating for [ 450 degree-Cx ] 10 minutes and repeating this actuation a total of 3 times. It carried out by performing heat treatment for [ 750 degree-Cx ] 30 minutes. The result of having measured the surface electrical resistance of the obtained oxide thin film is also written together to Table 1.

0032]

Table 1]

区分	No.	液中金属濃度 (%)			水分 (%)	x 値	沈澱発生の有無	薄膜の表面抵抗
		La	Sr	Co				
本発明例	1	1.0	5.7	4.2	0.7	0.1	無	$1 \times 10^{-1}$
	2	3.8	9.6	8.1	0.5	0.2	無	$5 \times 10^{-2}$
	3	6.0	8.9	8.5	0.3	0.3	無	$2 \times 10^{-2}$
	4	8.0	7.6	8.5	0.8	0.4	無	$2 \times 10^{-3}$
	5	2.0	1.3	1.7	0.9	0.5	無	$1 \times 10^{-4}$
	6	1.0	0.6	0.8	1.0	0.5	無	$1 \times 10^{-4}$
	7	6.0	2.5	4.2	0.8	0.6	無	$1 \times 10^{-3}$
比較例	8	<u>9.0</u>	5.7	7.6	0.9	0.5	有	$3 \times 10^{-4}$
	9	<u>11.0</u>	<u>10.4</u>	<u>11.7</u>	0.8	0.4	有	$5 \times 10^{-3}$
	10	4.0	0.6	2.1	0.8	<u>0.8</u>	有	$8 \times 10^{-3}$
	11	4.8	3.0	4.1	<u>1.5</u>	0.5	有	$3 \times 10^{-1}$

0033] As shown in Table 1, precipitate did not occur that the concentration of each carboxylate of La, Sr, and Co in a solution was [ moisture concentration ] 1 or less % of the weight in less than [ La:8 % of the weight ], less than [ Sr:10 % of the weight ], and less than [ Co:10 % of the weight ] during three-month storage, but the solution was able to be saved at stability for a long period of time. When such concentration exceeded at least one upper limit, the stability of a solution falls, and precipitate had occurred and it was impossible on the other hand, to use a solution during the storage which is three months, as shown in the example of a comparison.

0034] x values about surface electrical resistance 0.1-0.6 It turns out that the oxide thin film of enough low resistance is obtained by

within the limits. In addition, although surface electrical resistance was measured also about the oxide thin film which formed membranes similarly about the example of this invention using the solution after three-month neglect, surface electrical resistance was having been shown in Table 1, and this level.

[035]

Effect of the Invention] Stability is improved by this invention and the solution for LaSrCo multiple oxide thin film formation in which prolonged preservation is possible is obtained, without producing precipitate. Even after keeping this solution at a long period of time, it can form the same LaSrCo multiple oxide film of low resistance as storage before. Therefore, by this invention, a wet method enables it to stabilize a LaSrCo multiple oxide thin film and to form membranes, and membranous dependability increases. Moreover, the utility of an expensive solution decreases and membrane formation cost falls.

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(71)出願人 000006264

三菱マテリアル株式会社

東京都千代田区大手町1丁目5番1号

(72)発明者 森 暁

兵庫県三田市テクノパーク12-6 三菱マ

テリアル株式会社三田工場内

(72)発明者 曾山 信幸

兵庫県三田市テクノパーク12-6 三菱マ

テリアル株式会社三田工場内

(74)代理人 100081352

弁理士 広瀬 章一

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## (54)【発明の名称】 酸化物薄膜形成用溶液

## (57)【要約】

【課題】 沈殿を生じずに長期間安定に保存できる、LaとSrとRuを含む複合酸化物薄膜〔例、 $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$  ( $0.1 \leq x \leq 0.6$ )〕の湿式成膜用の溶液を提供する。

【解決手段】 有機溶媒中にランタンとストロンチウムとコバルトのそれぞれカルボン酸塩を含有する溶液からなり、溶液中の各金属の濃度がLa: 8重量%以下、Sr: 10重量%以下、Co: 10重量%以下であり、かつ溶液の水分濃度が1重量%以下である、LaSrCo複合酸化物薄膜形成用溶液。



る。この複合酸化物は、LaとSrとCo以外に、他の金属元素も少量であれば含有する。含有させる他の金属元素の例としてはCe、Pr、Nb、Rh、Irが挙げられる。

【0012】LaSrCo複合酸化物は、一般に低抵抗の導電性材料であるので、この複合酸化物の薄膜は酸化電極として機能する。しかし、本発明においては、薄膜の用途は特に制限されない。電極以外に、電極と強誘電体キャパシタとの間に介在させるバリア層といった、他の用途に使用することもできる。

【0013】好ましい複合酸化物は、金属元素がLaとSrとCoのみからなるものである。このような複合酸化物は、一般に $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$  ( $0 < x < 1$ ) なる式で表すことができるが、本発明では $x$ 値を0.1～0.6の範囲とする。 $x$ 値が0.1未満または0.6超になると、液の貯蔵安定性が低下し、保管中に沈殿が発生し易くなる。なお、 $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$ 膜において、 $x$ 値の変動により一般に薄膜の表面抵抗は $10^{-4} \sim 10^{-1} \Omega \cdot \text{cm}$ の範囲内で変動する。

【0014】本発明の酸化物薄膜形成用溶液は、成膜すべき複合酸化物を構成する各金属、即ち、LaとSrとCoの酸化物前駆体を含有する。酸化物前駆体は加熱により酸化物に変化する化合物である。一般のこの種の酸化物前駆体としては、金属アルコキシド、金属アセチルアセトナト錯体、金属カルボン酸塩等がよく使用されているが、本発明では、LaとSrとCoのいずれについてもカルボン酸塩を使用する。アルコキシドやアセチルアセトナト錯体を使用すると、液保管中に沈殿が発生しやすくなる。

【0015】各金属の酸化物前駆体として使用するカルボン酸塩は特に制限されないが、炭素数1～10のカルボン酸の塩、例えば、酢酸塩、プロピオン酸塩、酪酸塩、ヘキサン塩、2-エチルヘキサン塩、オクタン酸塩、デカン酸塩などが好ましい。La、Sr、Coのどの金属についても、特に好ましいカルボン酸塩は、比較的低温で熱分解する2-エチルヘキサン酸塩である。

【0016】原料の各金属の酸化物前駆体、即ち、LaとSrとCoの各カルボン酸塩（場合により他の金属の酸化物前駆体も使用できる）を、所定の金属原子比（即ち、 $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$ で示され、 $x$ が0.1～0.6の範囲内）を生ずるモル比で適当な有機溶媒に溶解させると、酸化物薄膜形成用溶液が得られる。

【0017】有機溶媒としては、アルコールやケトンといった水混和性の溶媒も使用できるが、好ましいのは炭化水素系溶媒のような水不混和性の有機溶媒である。好ましい有機溶媒の例としては、ベンゼン、トルエン、キシレン等の芳香族炭化水素類、ヘキサン、オクタン、シクロヘキサン等の脂肪族もしくは脂環式炭化水素類などが挙げられる。

【0018】しかし、原料の金属カルボン酸塩を所定比率で単に有機溶媒に溶解させただけでは、得られた溶液

は安定性に乏しく、短期間のうちに沈殿が生成して成膜に使用できなくなる。そのため、本発明では、溶液中の各金属化合物の濃度と、水分濃度を制限する。即ち、溶液中のLaとSrとCoの各カルボン酸塩の濃度を、金属換算の含有量として、La：8重量%以下、Sr：10重量%以下、Co：10重量%以下とし、かつ溶液の水分濃度が1重量%以下にする。この金属濃度は、好ましくはLa：2重量%以下、Sr：3重量%以下、Co：3重量%以下である。溶液中の水分濃度は好ましくは0.5重量%以下とする。溶液中の各金属濃度のいずれか、または水分濃度が上記の上限を超えると、溶液の安定性が低下し、長期保存が難しくなる。

【0019】各金属カルボン酸塩の濃度は、有機溶媒の使用量（即ち、有機溶媒による希釈度）により容易に調整できる。水分については、原料の金属カルボン酸塩が一般に結晶水を持つため、これを溶解した溶液はカルボン酸塩の結晶水に由来する水分を含有する。さらに、有機溶媒が、例えばアルコールやケトンのように水混和性が高い溶媒である場合には、放置しておくとき空気中の水分を吸収して、溶液の水分濃度が増大する。従って、このような原因で溶液中に混入する水分を除去することになる。

【0020】原料の金属カルボン酸塩からその結晶水等により溶液中に導入される水分を除去して溶液を脱水するには、原料の金属カルボン酸塩を有機溶媒に溶解させた後、好ましくは減圧下で加熱して水を蒸発または蒸留により除去すればよい。この場合、有機溶媒としては、水より沸点が高いものを使用することが好ましい。この加熱は、還流を行わずに濃縮させつつ行ってもよいが、有機溶媒が水不混和性の場合には、還流加熱により（即ち、留出物から水を分離した後に残る有機溶媒を還流させて）行うこともできる。加熱時間は、水分がほぼ完全に除去されるように設定する。

【0021】このようにして脱水した金属カルボン酸塩の溶液を、必要に応じて有機溶媒で希釈して濃度を調整する。原料の金属カルボン酸塩の溶解と希釈に使用する有機溶媒は、前述したように、水不混和性のものが好ましい。アルコールで代表される水混和性の有機溶媒は、保管中や使用中に水分を吸収しやすく、溶液が不安定になり易いからである。

【0022】本発明に係る酸化物薄膜形成用溶液は、密栓して保存すれば数カ月ないし1年またはそれ以上の長期にわたって、実質的に沈殿を生ずることなく安定に保存することができる。従って、この溶液を用いてゾルゲル法に準じて手軽にLaSrCo複合酸化物の薄膜を成膜することができる。

【0023】成膜操作は、従来のゾルゲル法と同様でよい。まず、基体上に上記溶液を塗布する。塗布は、スピンコート法により行うのが普通であるが、ロール塗布、噴霧、浸漬、ドクターブレードなど他の塗布法も適

に、溶液の安定性が低下し、3カ月の保管中に沈殿が発生しており、溶液を使用することができなくなっていた。

【0034】表面抵抗については、 $x$ 値が0.1~0.6の範囲内で十分に低抵抗の酸化物薄膜が得られることがわかる。なお、本発明例については、3カ月放置後の溶液を用いて同様に成膜した酸化物薄膜についても表面抵抗を測定したが、表面抵抗は表1に示したのと同レベルであった。

\*

## \*【0035】

【発明の効果】本発明により、安定性が改善され、沈殿を生じさせずに長期間の保存が可能な、LaSrCo複合酸化物薄膜形成用溶液が得られる。この溶液は、長期に保管した後も、保管前と同様の低抵抗のLaSrCo複合酸化物膜を成膜することができる。従って、本発明により湿式法によりLaSrCo複合酸化物薄膜を安定して成膜することが可能となり、膜の信頼性が高まる。また、高価な溶液の無駄が少なくなり、成膜コストが低下する。

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(72)発明者 影山 謙介

埼玉県大宮市北袋町1丁目297番地 三菱

マテリアル株式会社総合研究所内 ※

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